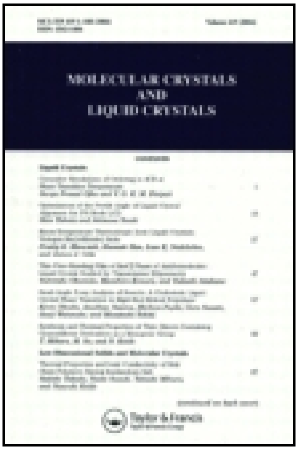


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# PARTIAL CASTING METHOD ON WATER SURFACE AND PREPARATION OF MULTI-CHANNEL SAW CHEMICAL SENSOR

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Abstract Surface acoustic wave (SAW) devices can be used as vapor phase chemical sensors. If we make use of SAW devices with high frequency properties and multi-channel structures, highly sensitive and multi gas sensors can be realized. However, it is generally difficult to deposit different gas sensitive films on the propagation paths of monolithic multi-channel SAW devices. This paper describes the new coating method by which several types of gas-sensitive molecular films can be coated on the paths. The method is called "partial casting method on water surface". It makes use of the water surface segmented by a trapezoidal frame, and the molecular film spread in the frame is compressed by the vertical movement of the frame and deposited on the substrate placed on the frame top. Several bilayers of dialkyl polyion complex and dimyristoyl phosphatidyl ethanolamine were coated on 36°Y-X $LiTaO_3$ SAW delay line oscillators, and odor sensor characteristics were successfully measured. It was confirmed from the present experiments that the method can be applicable to fabrication of multi-channel SAW chemical sensors with various kinds of molecular films.

## INTRODUCTION

SAW technology has big features of easy preparations of high-frequency devices with mass production scale and highly-functional or multi-channel devices monolithically, utilizing solid-state-device technology. In addition, it can be applied to realization of various types of sensors, and chemical sensors are the most promising examples among them. In the chemical sensors, sensing films are deposited on the propagation paths of the surface waves, and the mass-loading effect and/or piezoelectric interaction are caused by the physical or chemical phenomena after chemicals of interest are caught within the films or at their surfaces. Those effects influence the SAW propagation velocity in a delay line or the frequency in a SAW resonator or oscillator.

SAW chemical sensors usually have plural propagation paths. The simplest device is composed of the sensing channel with a sensing film and the reference one without any film on it. If the phase difference between the SAW signals propagating on those two channels is detected, the information just originating from the effects caused by the film can be obtained cancelling electrical noise or temperature drift occuring in both channels simultaneously. Moreover, chemometric sensors substantially need plural sensing channels. The typical sensors are the gas or odor sensors, which have low but slightly different specificities toward objective gas or odor, and the kind of gas or odor is recognised from the pattern of the output signals from those sensors. This technique shows significant advantages for gas or odor sensors. In case of gas sensors, many interesting gas signals are involved in addition to an objective gas because of a low specificity of the sensor (or the sensing film in a SAW sensor). The detection of multifarious molecular species are inevitable for odor identification, and an odor kind is identified from the overall balance of the signals that are output from the sensor array. SAW sensors with multi channels integrated monolithically and with different sensing films on them are considerably suitable for chemometric gas or odor sensors.

However, there exist a big difficulty for realizing that structure. Sensing films are deposited on SAW devices by various methods such as casting method, PVD method, etc. Although molecular films like LB films are appropriate for realizing sensors with quick responses and with biomimetic properties, there are no smart and efficient ways for depositing different LB films on the plural and very small SAW channels. This paper describes the new coating method by which several different kinds of gas-sensitive molecular films can be deposited on the channels. This method is named as "partial casting method on water surface". Several bilayers of dialkyl lipid were coated on SAW devices, and it was confirmed from the sensing experiments to odors that the method can be applicable to fabrication of chemometric SAW sensors to gas or odor.

## PARTIAL CASTING METHOD AND LIPID MATERIALS

LB method is prominent to deposit an organic film with the molecular-order thickness of wafer-scale uniformity, which is assured by a large spreading force of the solvent on water surface, the amphiphilic property of the solute molecule and the

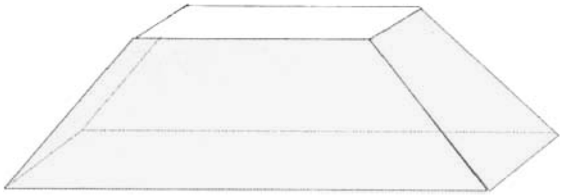

Figure 1: Trapezoidal frame made of stainless steel used in partial casting method on water surface.
frame top:10mm×5mm, frame bottom:30mm×5mm, and height:20mm

molecular compression due to the horizontal movement of the barrier on water surface. The spreading force gives rise to a good scattering of the molecular location on water surface in gas phase, and the amphiphilicity and the horizontal compression assure the good packing of oriented lipid molecules. In spite of that advantage, many engineers are not satisfied with LB method, because there is no technique for patterning a LB film. One of the present authors, T.M., has been emphasizing the importance of this technique [1][2]. The present paper demonstrates the first concrete and practical method for patterning molecular films, though the film is not a LB one according to an exact terminology.

The present method makes use of the water surface segmented by a trapezoidal frame (shown in Fig. 1), and the molecular film spread in the frame is compressed by the vertical movement of the frame. The compression ratio was about three when the frame shown in Fig. 1 was used. The film with a rectangular shape is finally deposited on the substrate placed on the frame top, though some part of the deposited molecular film is peeled to go back onto the water surface. The serial phenomena during the deposition process are illustrated schematically in Figs. 2 (a) to (c) for the case of a hydrophobic substrate.

The concentration of the spread solution and the compression ratio make a significant influence on the uniformity of the film thickness. If the concentration was high and the ratio low, some part of the spread material crystallized on the subphase, giving rise to a very rough film surface. Hence, it is required that the spread film in the stage of Fig. 2 (a) is in a gas or liquid phase on the subphase, and is compressed by the movement of the frame to have the structures of mono-molecular to several molecular layers in the stage of Fig. 2 (b). For another requirement, the inside

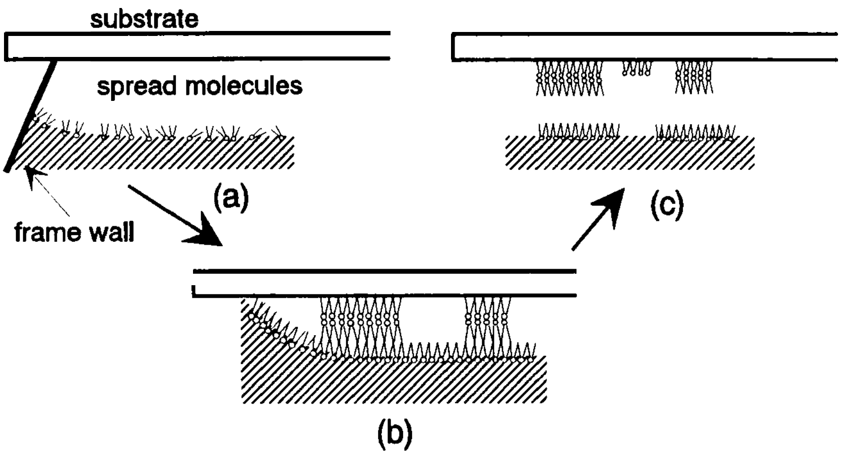


Figure 2: Schematic diagram of the molecular model predicted in the present method.
(a) Molecules are spread on water surface.
(b) Molecular films are made contact with a substrate by the compression.
(c) One cycle of the deposition is finished after water surface is lowered.

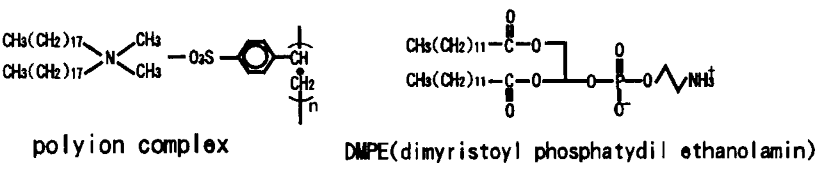


Figure 3: Molecular structures of lipid materials used in the present study.

surface of the frame must be made hydrophilic in order to keep the contact angle small enough to prevent the spread material from attaching to the frame wall. That condition was satisfied by making the frame of stainless steel.

The lipid materials used in the present study were a polyion complex synthesized in Prof.Y.Okahata's lab. [3] and DMPE (dimyristoyl phosphatidyl ethanolamine) purchased from Funakoshi Co. Both molecular equations are shown in Fig. 3.

## ELLIPSOMETRIC MEASUREMENT

After solving the polyion complex in chloroform (0.8mM) and dropping 1 $\mu$L of the solution onto the water surface inside the frame, one bilayer of the material was

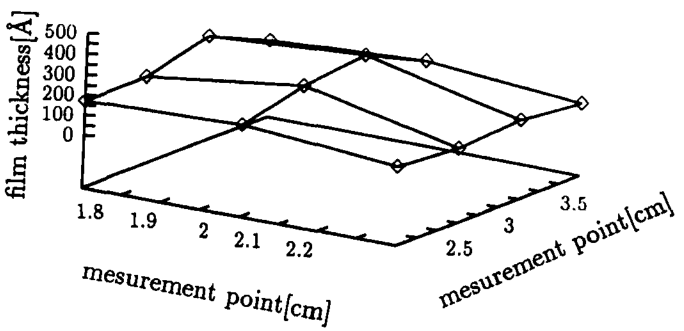


Figure 4: Spatial distribution of film thickness deposited on a $SiO_2/Si$ substrate.

thought to be formed after the compression (whose case is designated as "bilayer compression"), and transferred to the surfaces of $SiO_2/Si$ wafers with the oxide thickness of 5000Å. Repeating the above deposition cycles several times, the films were measured by an ellipsometer (EL-101,Nippon Infrared Co.). The distributions of the deposited thicknesses as a function of x-y coordinates on the wafers are shown in Fig. 4 for the films grown by 5 repetitive depositions. The variation of the thicknesses were about 50%. The thickness uniformity was better (variation of about 10%) if monolayers were formed after the compression (so-called "monolayer compression").

## SAW DEVICE FABRICATION AND THEIR PROPERTIES

### Influence Due to Film Deposition

The molecular film of the polyion complex was deposited on the SAW resonator shown in Fig. 5, which has an IDT with two reflectors on both sides of it, and the resonance frequency of 90 MHz. The deposition was done after making the device surface hydrophobic by silanization. The change of the resonance frequency as a function of the deposition number was measured, and the results for the two devices prepared by monolayer- and bilayer-compression methods are shown in Figs. 6 (a) and (b). In both cases the theoretical frequency changes were estimated from Wohltjen's equation [4], assuming that the full number of molecular layers were kept on

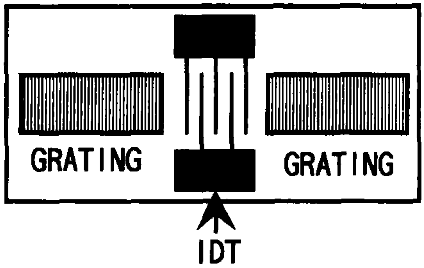


Figure 5: Configuration of SAW resonator. The film was deposited on whole the surface.

the device surfaces without losing any part of the films during the process. There found are large differences between the experimental and theoretical plots. The results mean that some part of the spread film material is lost during the compression, deposition and substrate-separation (from water surface) stages (shown in Fig. 2). In spite of the differences, the frequency change was clearly and reproducible proportional to the deposition number. This fact means that the present method is applicable and reliable for the molecular film deposition.

## Odor Sensing

The ultimate goal of authors' study is to realize multi-channel SAW sensors by the present deposition method. For a preliminary experiment toward it, 3-channel SAW delay lines with a center frequency of 30 MHz were prepared on a 36°Y–X $LiTaO_3$ wafer (Fig. 7). The central channel was used for a reference one without any film on it, and the bottom and top ones were coated with the polyion complex and DMPE by the present method. Each of the channels was connected with a wide-band amplifier to form an oscillator, and the oscillation frequency was measured by a counter.

The 3-channel sensor was installed in the temperature-stabilized vessel with a volume of 1.1L, and liquid odor samples were injected into it. The samples were 4 kinds of odors with same number of carbon atoms and with different odorous atomic groups; i.e., alcohol, aldehyde, ketone and ester. After vaporization of the samples and confirming the output stabilization, the sensor outputs were taken from the frequency differences between the reference signal and those of the coated channels,

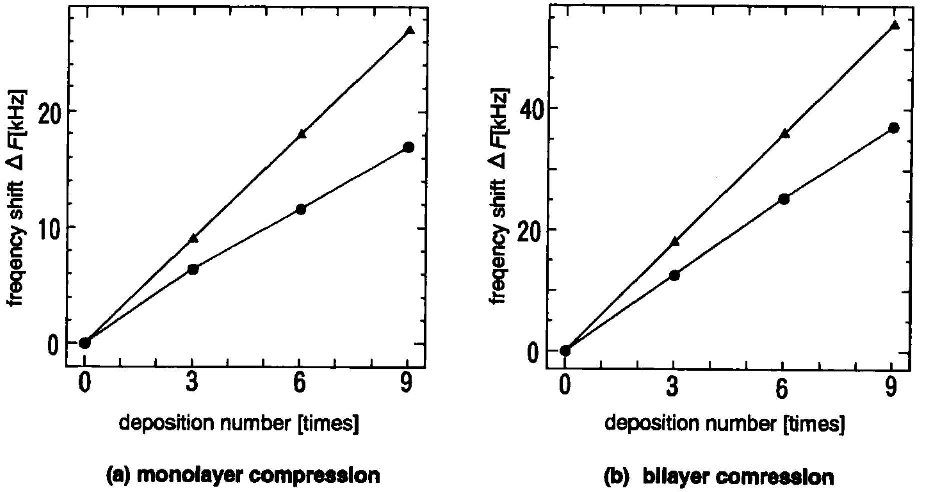


Figure 6: Resonance frequency changes as a function of the number of molecular film depositions.
The triangular and circular plots are theoretical and experimental ones, respectively.

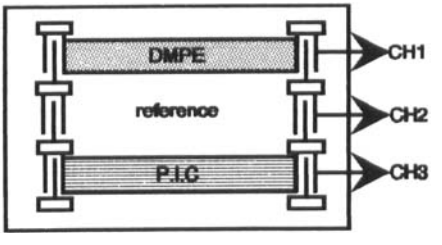


Figure 7: Configuration of three-channel SAW delay lines used for odor detection.

and is shown in Fig. 8. It is found that different odors gave different outputs to those sensors.

## CONCLUSION

Though only two odor sensors were used in the present experiment, the possibility of "partial casting method" for constructing multi-channel SAW chemical sensors were confirmed, and the preparation technique of biomimetic and chemometric odor or gas sensors has been advanced by the present study.

The yield of the deposition (the ratio of number of molecules deposited on a substrate to that of molecules spread on water surface) was not changed for both

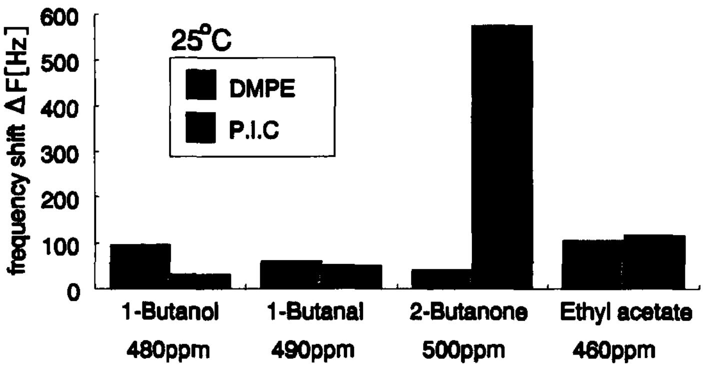


Figure 8: Sensor output pattern (frequency changes of SAW oscillators ) to 4 kinds of odor vapors.

monolayer and bilayer compressions. Though the exact deposition mechanism has not been made clear, the experimental results encourage us considerably because of its engineering significance. The study on its molecular mechanism goes on by a microscopic observation of the deposition and AFM or ellipsometric measurments.


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